Hydrogen Isotherms for $LaNi_{4.6}M_{0.4}$ Alloys where M=Group 4A Elements.

S. Luo, Ted B. Flanagan
Material Science Program and Department of Chemistry,
University of Vermont, Burlington VT 05405,
R. C. Bowman Jr
Jet Propulsion Laboratory,
California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109

Abstract

Hydrogen isotherms have been measured for activated $LaNi_{4.6}M_{0.4}$ alloys from 300 K to 473 K or 493 K where M= Si, Ge, Sn. Thermodynamic parameters have been obtained from the isotherms using van't Hoff plots for hydride formation and decomposition. The ΔH_{plat} values are more exothermic than for the parent compound, $LaNi_5$, but the ΔS_{plat} values are similar.

As for the $LaNi_{5-x}Sn_x$ alloys, $LaNi_{4.6}Ge_{0.4}$ and $LaNi_{4.6}Sn_{0.4}$ have a greater resistance towards degradation than the parent compound.

Introduction

It is well known that $LaNi_5$ degrades during continued hydriding/dehydriding at elevated temperatures, e.g., [1]. In an effort to have AB_5 alloys with greater resistance towards degradation than $LaNi_5$, a series of $LaNi_{4.6}M_{0.4}$

alloys have been prepared and characterized by isotherm measurements with M=Si, Ge and Sn.

It has been shown previously that M=Sn alloys have lower plateau pressures and a greater resistance to degradation than the parent compound, $LaNi_5$ [2, 3, 4, 5, 6]. Hysteresis for the activated forms of these alloys decreases significantly with increase of x. Other members of group 4A elements, i.e., Si and Ge, will be substituted into $LaNi_5$ in order to learn if they have desirable properties for H_2 storage with regards to plateau pressures and resistance towards degradation.

Previous research on these systems has been carried out by Mendelsohn *et al* [7] on all three of the $LaNi_{4.6}M_{0.4}$ alloys but only over a very limited temperature range, i.e., 303 K and 313 K, by Percheron-Guegan *et al* [8] for a $LaNi_{4.5}Si_{0.5}$ alloy at 303 K, by Witham *et al* [9] who determined isotherms at a few temperatures near ambient for a series of $LaNi_{5-x}Ge_x$ alloys and Meli *et al* measured dynamic H_2 isotherms at several temperatures for $LaNi_{4.7}Si_{0.3}$ and $LaNi_{4.5}Si_{0.5}$ alloys [10].

Experimental

The $LaNi_{4.6}M_{0.4}$ alloys were prepared at the Ames Laboratory of Iowa State University by arc-melting the elements. The purity of the Ni was 99.99% and the La 99.96% including *oxygen*. The buttons were melted several times inverting them after each melting. The arc–cast buttons were wrapped in Ta foil, sealed in an evacuated quartz tube and annealed at 1223 K for 100 h. The alloy ingots were shown to be single phase from metallography and the powder X–ray diffraction (XRD) patterns showed that the angles of the reflections were equal for randomly selected regions within the ingot.

The isotherms for the $LaNi_{4.6}Sn_{0.4}$ alloy had two sections in their plateaux which was not a "splitting" because these were exhibited for the initial absorption plateau. This is probably due to a gross inhomogeneity which could not removed by the annealing treatment. For this reason, another sample was also employed which had been obtained from HCl and had been employed earlier [4] which did not exhibit any anomalies.

Isotherms were measured in an all metal apparatus with electronic diaphragm gauges (M.K.S. Instruments). The temperatures were controlled with liquid baths to within ± 0.2 K.

Table 1: Lattice Parameters and Unit Cell Volume by XRD for the $LaNi_{4.6}M_{0.4}$ Alloys.

alloy	a_o/nm	c_o/nm	$V/nm^3/10^{-3}$
$LaNi_5$	0.5006	0.3993	86.75
$LaNi_{4.6}Si_{0.4}$	0.5023	0.3995	87.26
$LaNi_{4.6}Ge_{0.4}$	0.5036	0.4009	88.03
$LaNi_{4.6}Sn_{0.4}$	0.5091	0.4069	91.23
$LaNi_{4.8}Sn_{0.20}$	0.5057	0.4018	89.01

Results and Discussion

XRD Determination of Lattice Parameters.

The XRD patterns are shown in Figure 1 for unactivated, H-free alloys at 298 K. The results are shown in Table 1 where it can be seen that the lattice parameters and unit cell sizes increase in the order: $LaNi_5$, $LaNi_{4.6}Si_{0.4}$, $LaNi_{4.6}Ge_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$. The parameter and unit cell size for the $LaNi_{4.8}Sn_{0.2}$ are also shown and these are closer to the other $LaNi_{4.6}M_{0.4}$ alloys than the $LaNi_{4.6}Sn_{0.4}$ alloy. The lattice parameters for $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ do not differ very much but the latter parameters are definitely greater than the former.

Hydrogen Isotherms for $LaNi_{4.6}M_{0.40}$ at 373 K

An initial, activation isotherm is shown for the $LaNi_{4.6}Si_{0.4}$ alloy (373 K) with the subsequent isotherm and as usual for AB_5–H systems the initial absorption isotherm has a greater plateau p_{H_2} than the subsequent ones but the desorption plateau is nearly the same (Fig. 2). A total of 11 isotherms were measured on this alloy from 300 to 493 K.

An initial, activation isotherm is shown for the $LaNi_{4.6}Ge_{0.4}$ alloy (373 K) with the subsequent isotherm. As expected, the initial absorption isotherm has a greater plateau p_{H_2} than the subsequent ones and the desorption plateau is nearly the same. A total of 23 isotherms were measured with this alloy from 300 to 503 K. Some isotherms at 373 K are shown in Figure 3 where the activation absorption isotherm has only a few points but it has a

relatively greater absorption plateau than the subsequent ones as compared to the $LaNi_{4.6}Si_{0.4}$ alloy (Fig. 2).

Isotherms were measured for the $LaNi_{4.6}Sn_{0.4}$ alloys from both sources, Ames and HCI. The two had similar plateau pressures in the first half of their isotherms but the former had somewhat higher pressures in the latter half. Isotherms for the $LaNi_{4.6}Sn_{0.4}$ alloy from HCI were measured in 1992, 1995 and 1998 and, in each case, alloy from the arc-melted ingot was activated and a small decrease in the plateau pressures with time was noticed, i.e., an aging effect.

A series of isotherms at 373 K for each of the activated $LaNi_{4.6}M_{0.4}$ alloys, M=Ge and Sn, and for activated $LaNi_5$ are shown in Figure 4; the $LaNi_{4.6}Si_{0.4}$ alloy is not included because its isotherms are very close to those for the $LaNi_{4.6}Ge_{0.4}$ alloy. First of all, it can be seen that under identical conditions $LaNi_5$ shows plateau splitting but the other two do not; the desorption plateau splits for the initial, activation isotherm. The capacities of the $LaNi_{4.6}M_{0.4}$ alloys are smaller than for $LaNi_5$. The plateau pressures decrease from $LaNi_5$ to $LaNi_{4.6}Ge_{0.4}$ to $LaNi_{4.6}Sn_{0.4}$. The plateau pressures for $LaNi_{4.8}Sn_{0.2}$ are closer to the other $LaNi_{4.6}M_{0.4}$ alloys than are the pressures for $LaNi_{4.6}Sn_{0.4}$. This is not unexpected because the unit cell size for $LaNi_{4.8}Sn_{0.2}$ closer to the other $LaNi_{4.6}M_{0.4}$ alloys than the cell size of the $LaNi_{4.6}Sn_{0.4}$ alloy (Table 1).

Isotherms at various temperatures and van't Hoff plots for the $LaNi_{4.6}M_{0.40}$ alloys.

Figure 5 shows isotherms for activated forms of the alloys where the low temperature isotherms were carried out before the higher temperature ones and are therefore unaffected by any degradation which is not a significant factor in any case. There is a decrease in plateau widths as the temperatures are increased. At the higher temperatures the $LaNi_{4.6}Si_{0.4}$ alloy has greater plateau pressures than the $LaNi_{4.6}Ge_{0.4}$ alloy but at 300 K they have very similar plateau pressures. The enthalpy for hydride formation should be slightly greater for the former compared to the latter.

The corresponding van't Hoff plots are shown in Figure 6 for the $LaNi_{4.6}M_{0.4}$ alloys and they extend from 303 K to 373 K where only liquid temperature baths were employed. The derived thermodynamic parameters are tabulated in Table 2. The plateau enthalpies are as expected, i.e., more exothermic than for the parent compound, and the entropies are in the range expected

for AB_5-H systems, 54 ± 2 J/K mol $\frac{1}{2}H_2$, for the T-range centered about 350 K [4]. Values of the absorption parameters were determined by Mendelsohn *et al* [7] using isotherms from rather closely spaced temperatures and the results are ΔH^f_{plat}=−17.8, −17.1 and −19.2 kJ/ mol $\frac{1}{2}H_2$ for $LaNi_{4.6}Ge_{0.4}$, $LaNi_{4.6}Si_{0.4}$, and $LaNi_{4.6}Sn_{0.4}$, respectively and ΔS^f_{plat}=−57.1, −55.4 and −54.8 J/K mol $\frac{1}{2}H_2$ for the same alloys. No desorption values were determined. While the agreement with the present values are not bad, it is interesting that for the $LaNi_{4.6}Ge_{0.4}$ alloy the entropy change is more negative than the expected value of −54 ± 2 J/K mol $\frac{1}{2}H_2$ and consequently the enthalpy is also more negative than found here (Table 1), i.e., a somewhat anomalous entropy implies a spurious ΔH_{plat}.

If the equilibrium plateau pressure is taken as $\sqrt{p_f p_d}$ where p_f and p_d are the formation and decomposition plateau pressures [11] and ΔS_{plat} as 54 J/K mol $\frac{1}{2}H_2$ at ≈350 K, the plateau enthalpies can be calculated using

$$\Delta H_{calc,plat} = T(R \ln \sqrt{p_f p_d} - 54). \quad (1)$$

It is apparent that there is a temperature dependence in the calculated values because $|\Delta S_{plat}|$= 54 J/K mol $\frac{1}{2}H_2$ is the appropriate value at a temperature centered about 350 K, however, there is only a difference of 0.1 J/K mol $\frac{1}{2}H_2$ using data at 373 K or 323 K for these systems. It is clear from Table 2 that the calculated values are very close to the average of the $|\Delta H_{plat}|$ values for absorption and desorption making the approximate method quite convenient and probably more accurate than experimental values which may be based on a limited number of closely spaced sets of plateau pressures/temperatures.

The loss of work due to hysteresis can be computed from the expression

$$\frac{1}{2}RT \ln (p_f/p_d) \quad (2)$$

where p_f and p_d are the plateau pressures for hydride formation and decomposition, respectively. Using the expression for the loss of work, the hysteresis is about 150 J/ mol $\frac{1}{2}H_2$ (323 K) which is quite small; the value for the $LaNi_{4.6}Sn_{0.4}$ alloy is somewhat smaller than this but the hysteresis for the $LaNi_{4.8}Sn_{0.2}$ alloy. is about equal to this.

Table 2: Thermodynamic Parameters for $LaNi_{4.6}M_{0.4}$ Alloys and $LaNi_5$, $LaNi_{4.8}Sn_{0.2}$ where ΔH_{plat} is in units of kJ/ mol $\frac{1}{2}H_2$ and ΔS_{plat} is in units of J/ K mol $\frac{1}{2}H_2$.

alloy	ΔH^f_{plat}	ΔH^d_{plat}	$\lvert\Delta H_{calc,plat}\rvert$	ΔS^f_{plat}	ΔS^d_{plat}
$LaNi_5$	-15.1	15.3	15.3	-54.2	53.7
$LaNi_{4.6}Si_{0.4}$	-16.8	17.1	16.6	-54.8	55.2
$LaNi_{4.6}Ge_{0.4}$	-16.1	17.0	16.8	-52.2	53.9
$LaNi_{4.6}Sn_{0.4}$	-19.0	19.1	18.9	-54.3	54.4
$LaNi_{4.8}Sn_{0.20}$	-17.0	17.1	17.0	-54.6	54.2

Degradation of $LaNi_{4.6}M_{0.40}$ Alloys.

As shown by Sandrock *et al* [12] an effective test for stability is to hold an AB_5 alloy at a large H content at an elevated temperature, "soaking". After such soaking it was shown that $LaNi_{5-x}Mn_x$ alloys degraded rather quickly at 573 K [13]. The degradation was shown by the failure of the subsequent desorption isotherm to coincide with the absorption isotherm in the dilute phase, by slow kinetics and by subsequent anomalous isotherms at a lower temperature. In the parent compound system, $LaNi_5$, degradation is accompanied by plateau splitting [1].

The $LaNi_{4.6}M_{0.4}$ alloys resist degradation more effectively than either of the above which is the principal reason why the $LaNi_{5-x}Sn_x$ alloys have been used for practical applications, e.g., [14]. Luo *et al* [5] found that after the $LaNi_{4.8}Sn_{0.2}$ alloy was "soaked" at, e.g., 523 K for 72 h at 140 bar, there was no evidence for any degradation. The degradation of the $LaNi_{4.6}Sn_{0.4}$ alloy has not been examined until now.

The two different (Ames and HCl) $LaNi_{4.6}Sn_{0.4}$ samples were subjected to soaking, e.g., 523 K for 24 h at 103 bar, and in both cases the was no effect on the subsequent isotherms at 373 K except for a small lowering of the desorption plateau pressure.

Soaking the $LaNi_{4.6}Ge_{0.4}$ alloy at 118 bar for 24 h at progressively higher temperatures 473 K, 493 K did not cause any changes in the subsequent isotherms (373 K) measured after soaking at each temperature but there was a lowering of the plateau pressures after soaking at 503 K (Fig. 3).

The $LaNi_{4.6}Si_{0.4}$ alloy was soaked at 473 K for 15 h at 112 bar and

there was no change in the subsequent isotherm (373 K) except for a small decrease in p_d and increase of hysteresis (Fig. 2). This was also found for another sample "soaked" at the same temperature.

Conclusions

Isotherms have been measured and thermodynamic parameters determined for $LaNi_{4.6}M_{0.4}$ alloys. The $LaNi_{4.6}Si_{0.4}$ and $LaNi_{4.6}Ge_{0.4}$ alloy–H systems have similar plateau pressures while the latter has a slightly greater H capacity. Both have significantly greater plateau pressures than $LaNi_{4.6}Sn_{0.4}$--H. The $LaNi_{4.6}M_{0.4}$ alloys are quite resistant to degradation by "soaking" at elevated temperatures although there is a slight decrease of p_d for the $LaNi_{4.6}Sn_{0.4}$ and $LaNi_{4.6}Si_{0.4}$ alloys after soaking. Both p_f and p_d were $\approx$12% lower after a 503 K soaking, but there was no loss in capacity.

Acknowledgements

This research was partially supported by the Jet Propulsion Laboratory operated by California Institute of Technology under contract with the U.S. National Aeronautics and Space Administration. The authors are grateful to T. M. Riedemann and associates of Iowa State University for the preparation of the $LaNi_{4.6}M_{0.4}$ alloys.

References

[1] S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, *J. Alloys Comp.*, **253-254** (1997) 226.

[2] S. Lambert, D. Chandra, W. Cathey, F. Lynch, R. Bowman, *J. Alloys Compounds*, **187** (1992) 113.

[3] J. Cantrell, T. Beiter, R. Bowman, *J. Alloys Compounds*, **207** (1994) 372.

[4] S. Luo, W. Luo, J. Clewley, T. Flanagan, L. Wade, *J. Alloys Compounds*, **231** (1995) 467.

[5] S. Luo, W. Luo, J. Clewley, T. Flanagan, R. Bowman, *J. Alloys Compounds,* **231** (1995) 473.

[6] S. Luo, J. Clewley, T. Flanagan, R. Bowman, L. Wade, *J. Alloys Compounds,* **267** (1998) 171.

[7] M. Mendelsohn, D. Gruen, A. Dwight, *Inorg. Chem.,* **18** (1979) 3343.

[8] A. Percheron-Guegan, C. Lartique, J. Achard, *J. Less-Commnon Mets.*,**109** (1985) 187.

[9] C. Witham, R. Bowman, B. Fultz, *J. Alloys Comp.,* **253-254** (1997) 574.

[10] F. Meli, A. Zuettel, L. Schlapbach, *J. Alloys Comp.,* **190** (1992) 17.

[11] T. Flanagan, C.-N. Park, W. Oates, *Prog. in Solid State Chem.,* **23** (1995) 291.

[12] G. Sandrock, P. Goodell, E. Huston, P. Golben, *Zeit. Phys. Chem., N.F.,* **164** (1989) 1285.

[13] W. Luo, S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, *J. Alloys Compounds,* **202** (1993) 147.

[14] R. Bowman, P. Karlmann, S. Bard, *Brilliant Eyes Ten- Kelvin Sorption Cryocooler Experiment,* JPL Publication 97-14, 1997.

Fig. 1 XRD patterns for H-free, unactivated $LaNi_{4.6}M_{0.4}$ alloys (298 K); the reflections appear rather broad because of the narrow 2θ scale. The three different alloys are identified on the Figure.

Fig. 2 Hydrogen isotherms for the $LaNi_{4.6}Si_{0.4}$ alloy at 373 K. $\diamond$, isotherm for unactivated alloy; $\triangle$, second isotherm; $\square$, measured after an isotherm measured and "soaked" at 473 K, 15 h at 112 bar. Open symbols represent absorption and filled ones desorption.

Fig. 3 Hydrogen isotherms for the $LaNi_{4.6}Ge_{0.4}$ alloy at 373 K. $\diamond$, isotherm for unactivated alloy; $\triangle$, second isotherm; $\square$, measured after 9 previous cycles at temperatures and soaking at 473 K for 44 h at 116 bar

(H/AB_5= 3.5); ◯, isotherm after soaking at 493 K for 25 h at 118 bar (H/AB_5= 3.5); ▽, isotherm after at 503 K for 24 h at 110 bar. Open symbols represent absorption and filled ones desorption.

Fig. 4 Hydrogen isotherms for activated $LaNi_5$, $LaNi_{4.6}Ge_{0.4}$ and $LaNi_{4.6}Sn_{0.4}$alloys (373 K). The different symbols show different isotherms for each.

Fig. 5 Hydrogen isotherms for the $LaNi_{4.6}M_{0.4}$ alloys at different temperatures. Continuous curve without data points, $LaNi_{4.6}Sn_{0.4}$; – – – – without data points, $LaNi_{4.6}Ge_{0.4}$; △, $LaNi_{4.6}Si_{0.4}$.

Fig. 6 Van't Hoff plots for the $LaNi_{4.6}M_{0.4}$ alloys compared to $LaNi_5$ [6] and to $LaNi_{4.8}Sn_{0.2}$. The dotted lines without data points represent the van't Hoff plots for the $LaNi_{4.6}Ge_{0.4}$ alloy. Open symbols are for absorption and filled ones for desorption.

Fig. 1

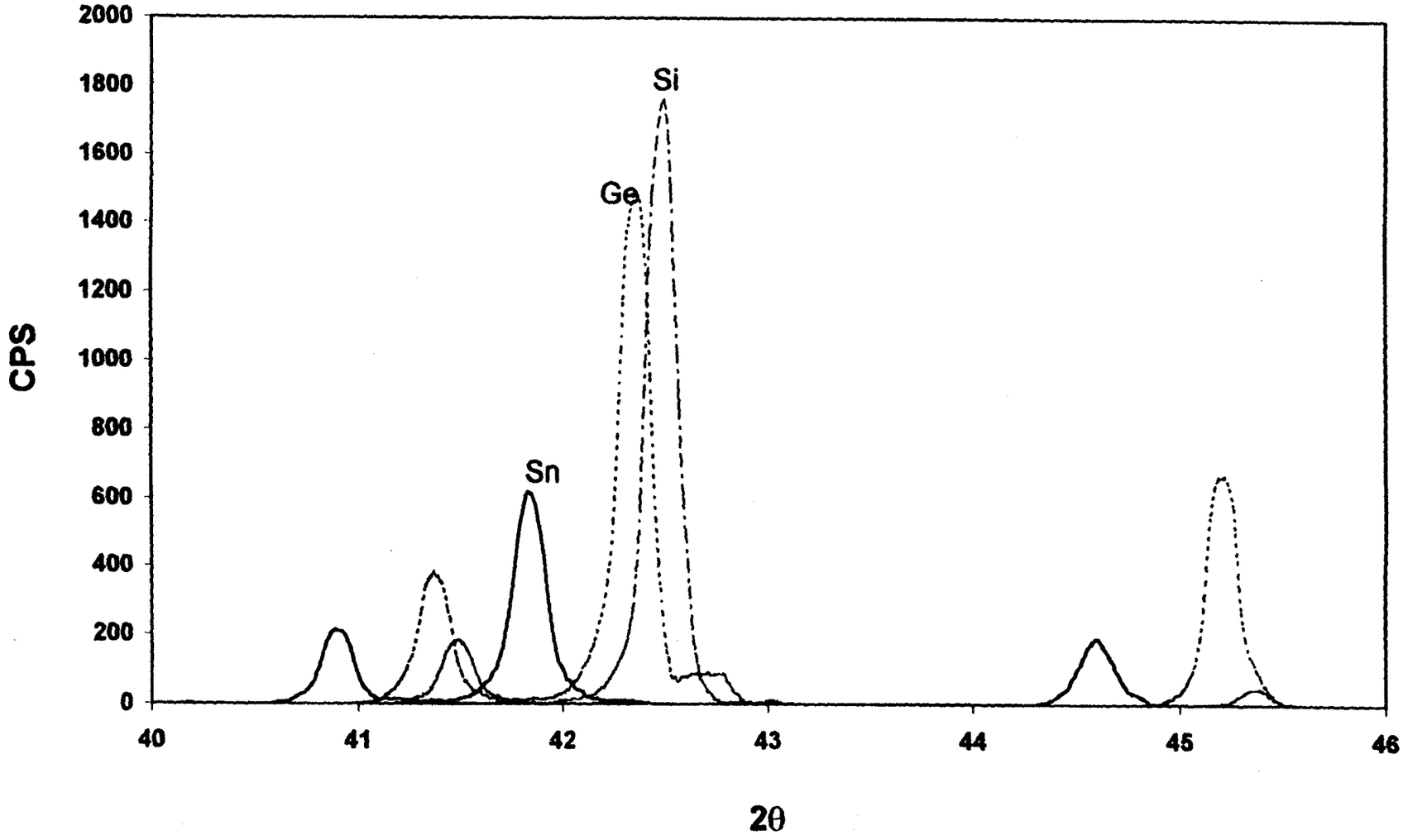

2000
1800
1600
1400
1200
1000
800
600
400
200
0
CPS
Si
Ge
Sn
40
41
42
43
44
45
46
2θ

Fig. 2.

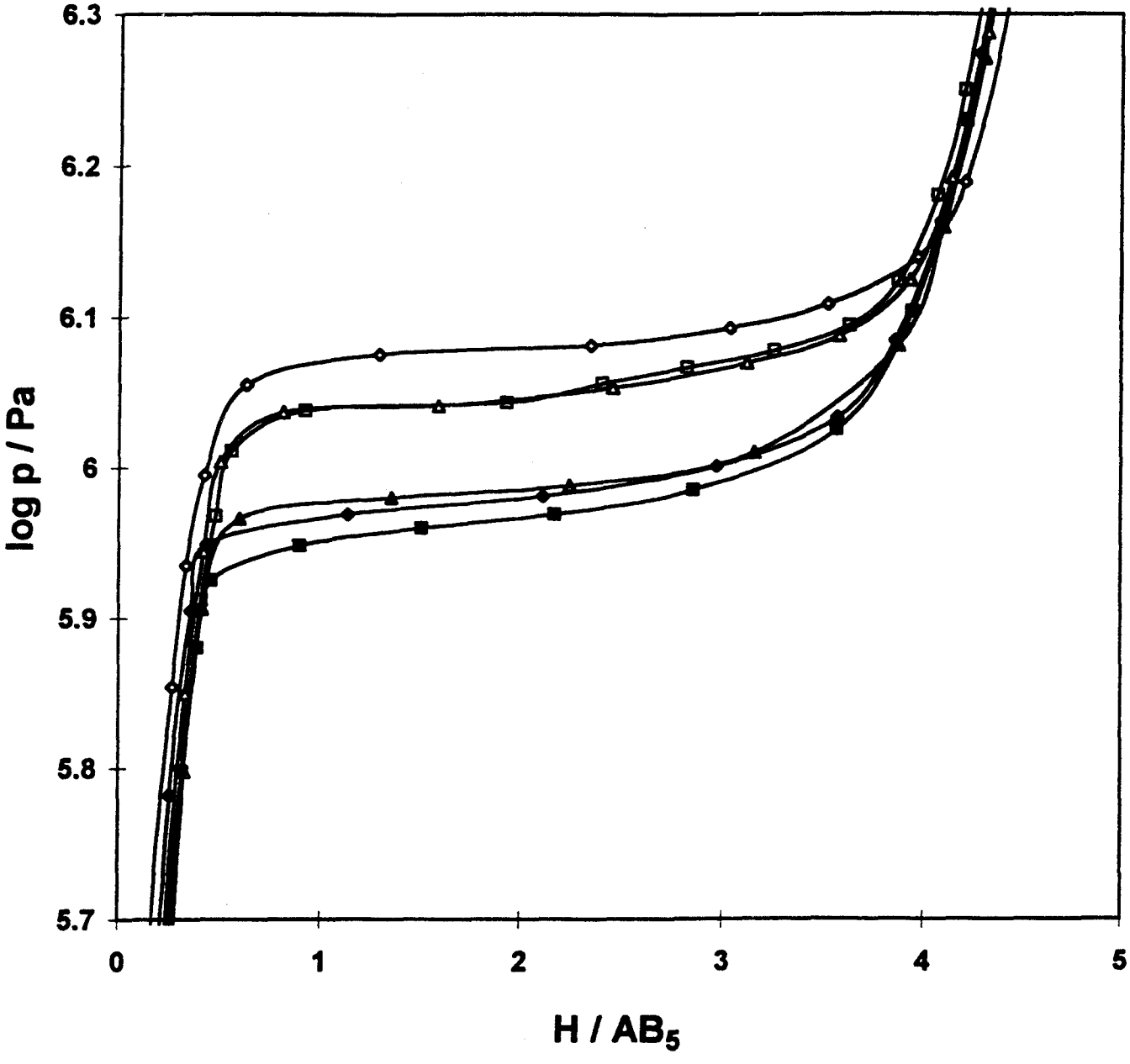


Fig. 3.

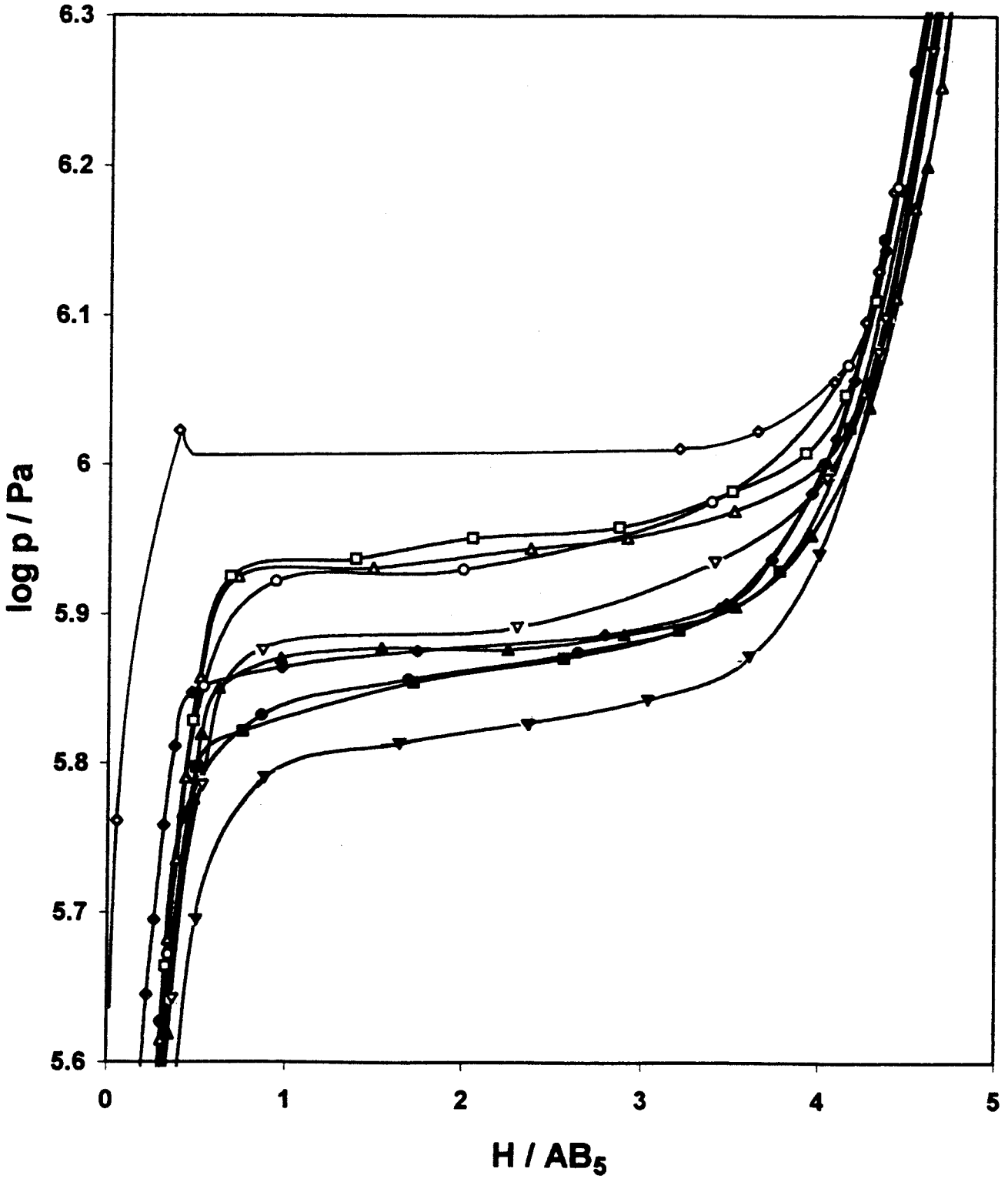


Fig. 4

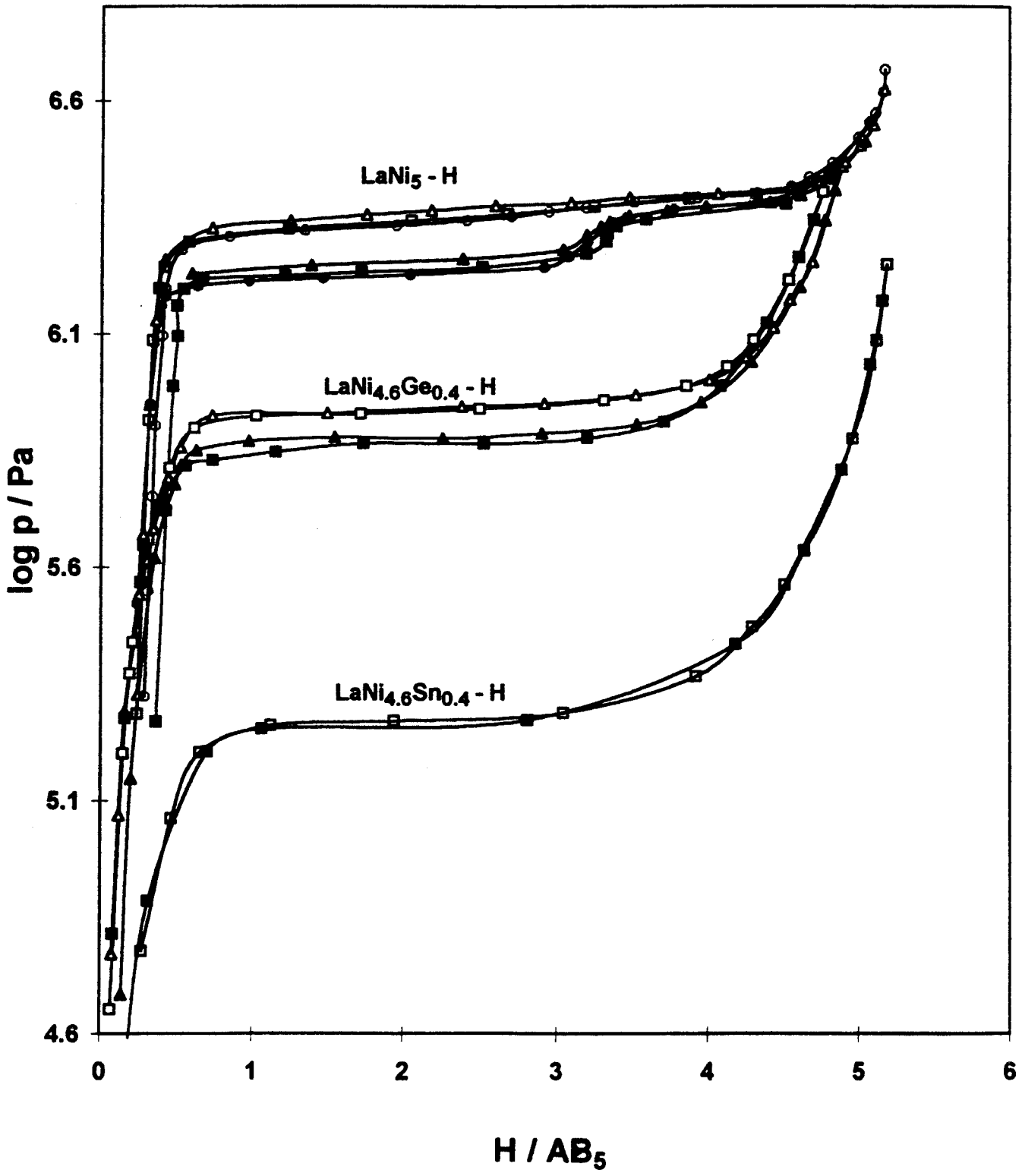

6.6
6.1
5.6
5.1
4.6
log p / Pa
LaNi5 - H
LaNi4.6Ge0.4 - H
LaNi4.6Sn0.4 - H
0
1
2
3
4
5
6
H / AB5

Fig. 5.

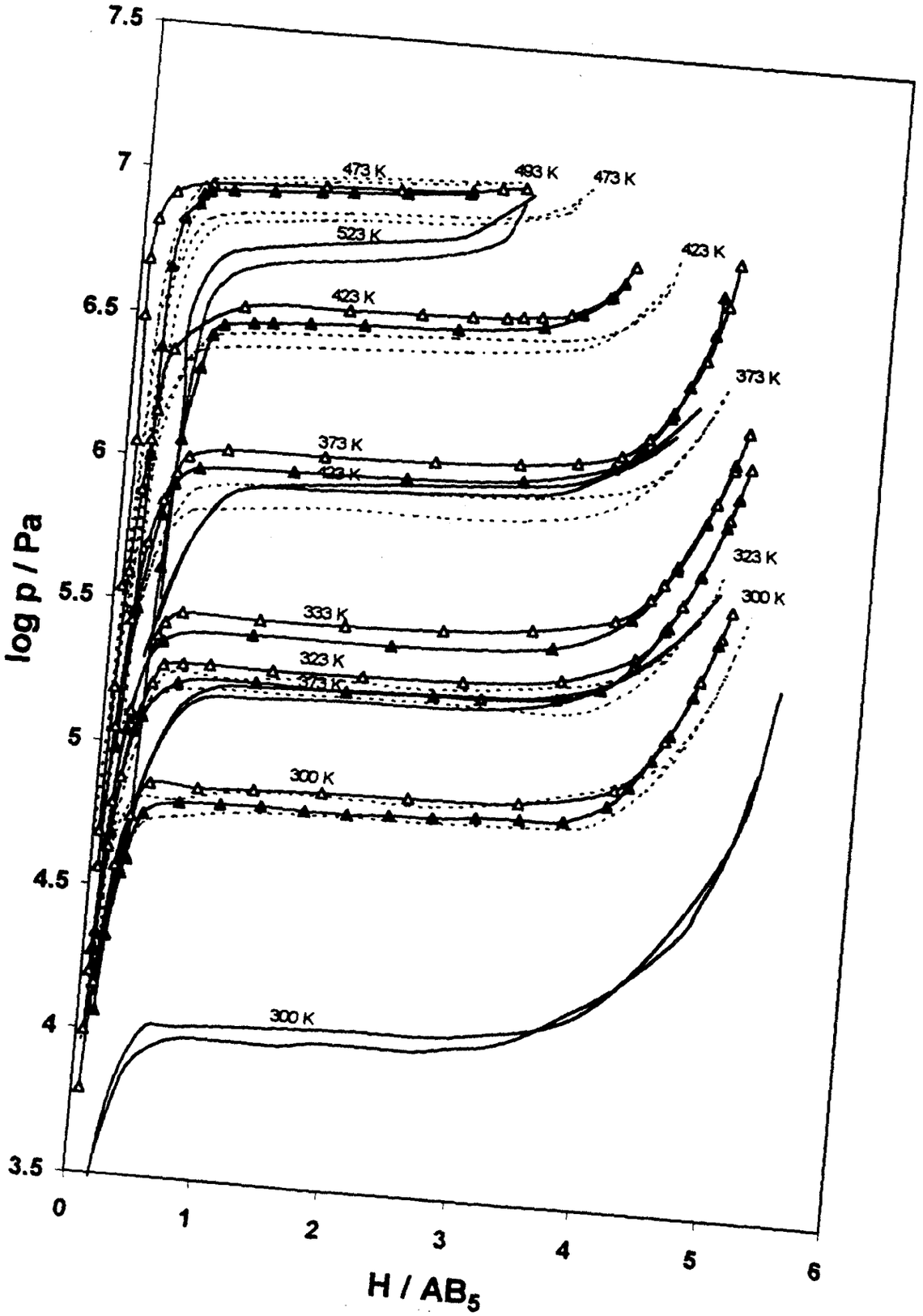
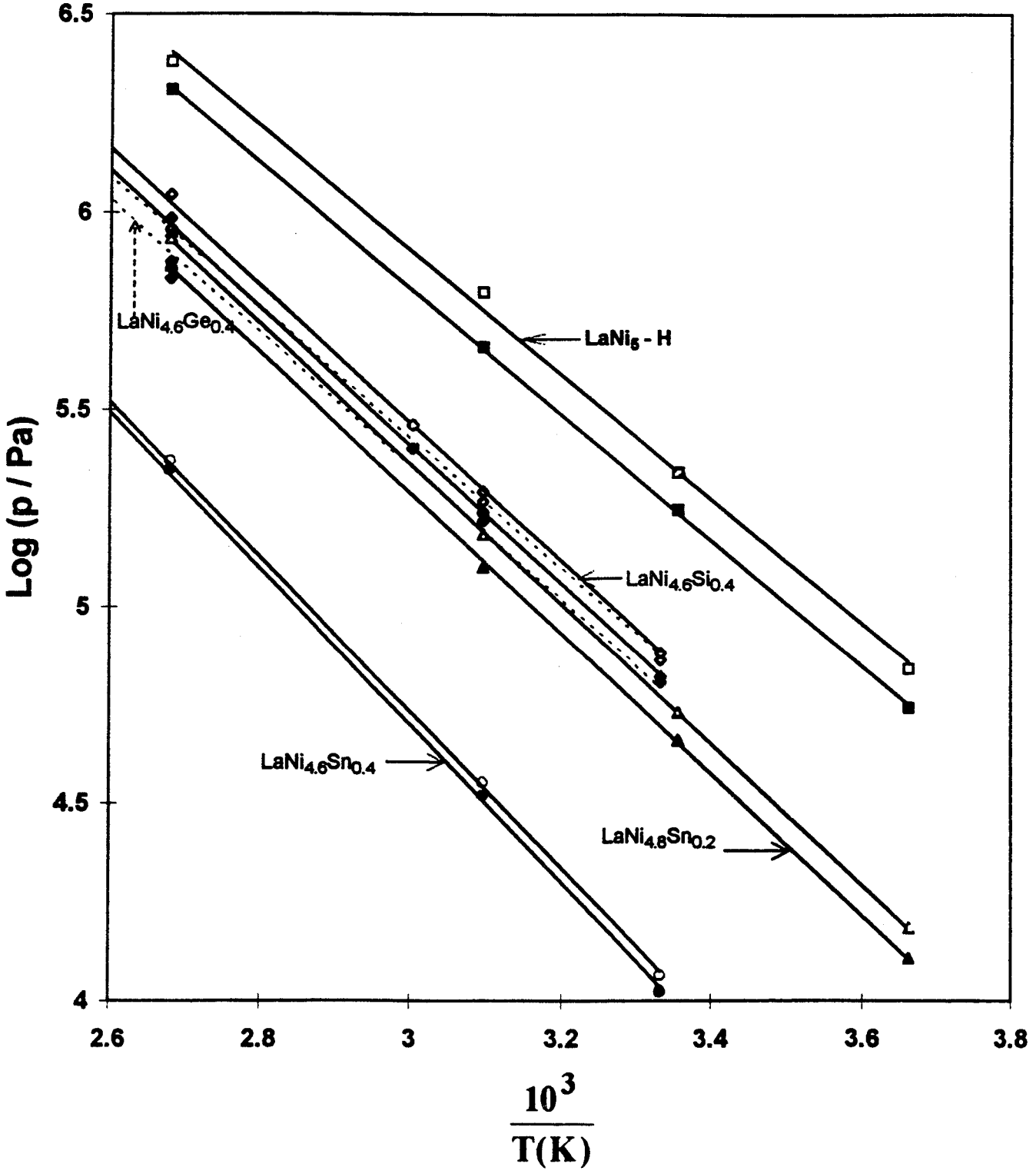

7.5
7
6.5
6
5.5
5
4.5
4
3.5
log p / Pa
0
1
2
3
4
5
6
H / AB5
473 K
493 K
473 K
523 K
423 K
423 K
373 K
373 K
423 K
323 K
333 K
323 K
373 K
300 K
300 K
300 K

Fig. 6.


6.5
6
5.5
5
4.5
4
Log (p / Pa)
2.6
2.8
3
3.2
3.4
3.6
3.8
10^3 / T(K)
LaNi4.6Ge0.4
LaNi5 - H
LaNi4.6Si0.4
LaNi4.6Sn0.4
LaNi4.8Sn0.2